

## PAPER

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[View Journal](#) | [View Issue](#)Cite this: *Catal. Sci. Technol.*, 2016,  
6, 8117Selective CO<sub>2</sub> methanation on Ru/TiO<sub>2</sub> catalysts:  
unravelling the decisive role of the TiO<sub>2</sub> support  
crystal structure†A. Kim,<sup>ab</sup> C. Sanchez,<sup>b</sup> G. Patriarche,<sup>c</sup> O. Ersen,<sup>d</sup> S. Moldovan,<sup>d</sup> A. Wisnet,<sup>e</sup>  
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The catalytic hydrogenation of CO<sub>2</sub> is a relevant strategy for mitigating CO<sub>2</sub> emissions and its applicability relies on our ability to prepare catalysts that are highly active under mild conditions. Understanding and improving these tailored catalysts requires innovative materials synthesis routes and advanced methods of characterization. In this study, mono-dispersed 2 nm RuO<sub>2</sub> nanoparticles were prepared as a stable colloidal suspension and deposited onto different titania supports by impregnation. Supported RuO<sub>2</sub> nanoparticles are homogeneously dispersed at the surface of the titania supports. Then, upon annealing and reduction, metallic Ru nanoparticles are obtained, which are active in the hydrogenation of CO<sub>2</sub> to CH<sub>4</sub>. However, depending on the crystal structure of the different TiO<sub>2</sub> supports (anatase, rutile, and a mixture of both), the catalysts exhibited drastically diverse catalytic performances. An array of characterization tools (N<sub>2</sub>-physisorption, H<sub>2</sub>-chemisorption, HR-TEM, STEM-HAADF, 3D tomographic analysis, XRD, and XPS) was used to unravel the origin of this support effect. It appeared that catalytic behaviour was related to profound morphological changes occurring during the annealing step. In particular, advanced electron microscopy techniques allow visualisation of the consequences of RuO<sub>2</sub> nanoparticle mobility onto titania. It is shown that RuO<sub>2</sub> sinters heavily on anatase TiO<sub>2</sub>, but spreads and forms epitaxial layers onto rutile TiO<sub>2</sub>. On anatase, large Ru chunks are finally obtained. On rutile, the formation of a particular “rutile-TiO<sub>2</sub>/RuO<sub>2</sub>/rutile-TiO<sub>2</sub> sandwich structure” is demonstrated. These phenomena – along with the relative thermal instability of the supports – explain why the catalysts based on the commercial P25 titania support outperform those based on pure crystalline titania. The study opens new perspectives for the design of highly active CO<sub>2</sub> methanation catalysts.

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## Introduction

Supported metal nanoparticles feature important structural properties that dictate their performance in heterogeneous catalysis.<sup>1–6</sup> Indeed, a structure–performance relationship is found in many metal-catalysed reactions.<sup>7–13</sup> Although the primary role of the support material is sometimes thought to be

limited to serving as a physical carrier for intact metal nanoparticles, it has been recognized that the chemical nature of the support or the metal–support interactions can have a marked impact on catalytic activities and/or selectivity.<sup>14,15</sup> Thus, the design of tailored supports for metal-based catalysts is a topical field of research which concerns the size, shape, texture, crystallinity, and redistribution process of the metal nanoparticles on their support.<sup>13,16,17</sup>

CO<sub>2</sub> hydrogenation to CH<sub>4</sub> (CO<sub>2</sub> methanation), also known as the Sabatier reaction, is an important catalytic process of fundamental academic interest with potential commercial application.<sup>18–20</sup> In the current environmental context, this reaction not only reduces CO<sub>2</sub> emissions but produces CH<sub>4</sub>, which can be directly transported through existing natural gas pipelines to be used as a fuel or as a chemical building block, simultaneously targeting both the valorisation of CO<sub>2</sub> (reduction of greenhouse gases) and the vectorization of dihydrogen via CH<sub>4</sub>.

Although CO<sub>2</sub> methanation has been a topical field of research for decades, the emphasis on the development in this

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area has only recently turned to catalytic performance with high selectivity at thermodynamically favourable conditions (*i.e.* low temperature and pressure) using different types of metals and supports.<sup>21</sup>

Reducible group VIII metal oxides have been widely used as support materials. Among them, TiO<sub>2</sub> is best known for its high stability, high ultraviolet absorption, and semiconductor properties which allow its use in various applications in catalysis and photocatalysis.<sup>22</sup> Furthermore, the existence of various crystalline phases of TiO<sub>2</sub> contributes to the tuning of catalytic performance in heterogeneous catalysis through morphologic and electronic perturbations.<sup>12,16</sup> For example, TiO<sub>2</sub> is known as the most efficient support for noble metal catalysts including Pd, Ru and Rh in CO and CO<sub>2</sub> methanation.<sup>21,23–25</sup> Recently, TiO<sub>2</sub> supported RuO<sub>2</sub> nanoparticles have shown excellent oxidation capability as Deacon catalysts displaying different stabilities depending on the crystalline phases of TiO<sub>2</sub>.<sup>13,26</sup>

A study on the crystal phase effect of TiO<sub>2</sub> on the structure and performance of Ru nanoparticles in CO<sub>2</sub> hydrogenation has been recently reported.<sup>12</sup> This study demonstrated the strong impact of the support crystal structure on Ru dispersion and therefore on methanation activity. In particular, rutile TiO<sub>2</sub> was identified as the most promising support; thanks to the strong interaction it can develop with RuO<sub>2</sub>. However, the catalysts were prepared by a conventional impregnation method (IM), and this does not provide good control over the initial RuO<sub>2</sub> dispersion, itself being a key parameter for the final Ru nanoparticle dispersion.

The impact of a structure–performance relationship in Ru-based catalysts has given rise to various preparation methods for well-dispersed and/or uniformly-sized nanoparticles of Ru and RuO<sub>2</sub> for many catalytic applications in hydrogenation and oxidation reactions.<sup>27–30</sup> Abe *et al.* have developed a dry technique for modifying the surfaces of powdery materials named as polygonal barrel-sputtering to prepare Ru nanoparticle loaded TiO<sub>2</sub> with a narrow particle size distribution without the need of any heating which can cause nanoparticle sintering.<sup>31</sup> Balaraju *et al.* have shown the superior catalytic performances of Ru/TiO<sub>2</sub> catalysts prepared by a deposition–precipitation (DP) method compared with those prepared by a conventional impregnation (IM) method in the hydrogenolysis of glycerol, which was attributed to the presence of well-dispersed nano-sized Ru particles on TiO<sub>2</sub>.<sup>32</sup> Also, Sassoye *et al.* have previously reported on the synthesis of mono-dispersed 2 nm RuO<sub>2</sub> nanoparticles in an aqueous colloidal suspension and the preparation of Ru/TiO<sub>2</sub> catalysts after reduction under H<sub>2</sub>.<sup>33</sup> Such catalysts demonstrated superior catalytic performance in CO<sub>2</sub> methanation compared to that prepared by an IM method.<sup>33</sup>

The successful preparation of a suspension of uniformly distributed 2 nm RuO<sub>2</sub> nanoparticles and the suspected structure–performance relationship in Ru-catalysed CO<sub>2</sub> methanation has prompted us to study the active phase–support interaction between pre-formed calibrated RuO<sub>2</sub> nanoparticles and TiO<sub>2</sub> supports with different crystalline phases.

Indeed, starting from well-defined dispersed RuO<sub>2</sub> nanoparticles, TiO<sub>2</sub> supports with different crystalline phases might favour the stabilization of Ru in different states of dispersion, shape, structure.

In the present work, RuO<sub>2</sub> nanoparticles of 2 nm were initially prepared by a colloidal method and supported on pure anatase, pure rutile, and P25 TiO<sub>2</sub>. The uniform size distribution of RuO<sub>2</sub> nanoparticles facilitated a more accurate study of the influence of the TiO<sub>2</sub> crystalline phases on RuO<sub>2</sub> nanoparticles and the resulting catalytic behaviour in CO<sub>2</sub> methanation. The morphological changes in the RuO<sub>2</sub> nanoparticles were monitored after various thermal annealing temperatures and correlated with the CO<sub>2</sub> methanation activity at low temperature ( $\leq 200$  °C) and one standard atmospheric pressure.

## Results and discussion

### Basic characterization of supports and catalysts

XRD analyses confirmed the structure of the supports alone; mixed anatase and rutile phases for P25 TiO<sub>2</sub>, the pure anatase phase for the home-made anatase TiO<sub>2</sub>, and the pure rutile phase for the home-made rutile TiO<sub>2</sub> (see the ESI† SI-1).

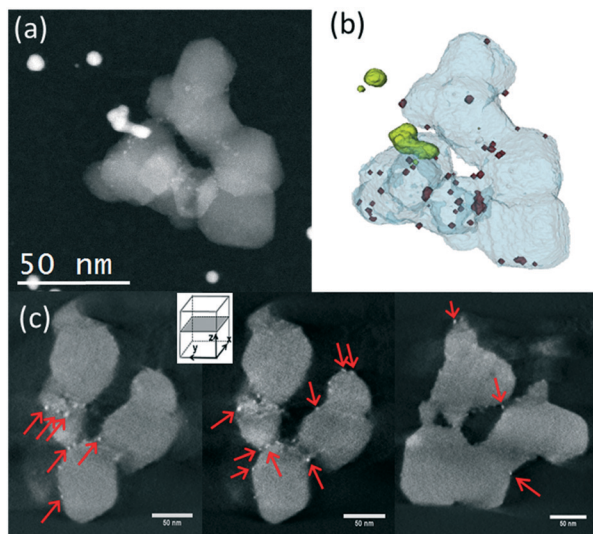
The 2D particle shapes of the three TiO<sub>2</sub> supports, namely, P25, anatase, and rutile, were distinctive and well distinguishable from one another as shown by direct TEM observations in SI-2.† P25 TiO<sub>2</sub> particles were rounded, rectangular-shaped, with anatase and rutile crystallites being impossible to distinguish; home-made anatase TiO<sub>2</sub> particles were a mixture of oval and rhombus shapes; and home-made rutile TiO<sub>2</sub> particles were needle-shaped. The particle sizes measured from TEM images were, on average, 25–30 nm for P25 TiO<sub>2</sub>, 6–7 nm for anatase TiO<sub>2</sub>, and 12 × 100 nm for rutile TiO<sub>2</sub>.

There was no difference in the shapes and sizes of the supports before and after the deposition of RuO<sub>2</sub> nanoparticles with annealing at 150 °C (SI-3a–c†). The RuO<sub>2</sub> nanoparticles have kept their initial ~2 nm diameter on all supports and appeared globally well dispersed as proven by the 2D TEM micrographs. The 3D-STEM-HAADF tomography images (Fig. 1) provide the ultimate proof of good dispersion of RuO<sub>2</sub> nanoparticles on the surface of P25 TiO<sub>2</sub>. To complement Fig. 1, a video showing the reconstructed volume with the catalyst particles deposited on the P25 TiO<sub>2</sub> support under rotation is available in the ESI† (SI-4).

ICP-AES elemental analysis of the catalysts (SI-5†) resulted in Ru contents of 2.35–2.60 wt%, indicating no Ru loss during the entire synthesis process (the small variation comes from the variation in the water content in the RuCl<sub>3</sub>·xH<sub>2</sub>O ( $x = 3–5$ ) precursor). The specific surface areas obtained by the BET method ( $S_{\text{BET}}$ ) before and after the deposition of RuO<sub>2</sub> followed by annealing at 150 °C were found to be consistent, as shown in Table 1.

In XPS, all 150 °C-annealed catalysts present Ru/Ti ratios that are higher than the 0.043 bulk Ru/Ti ratio (calculated based on the 2.5 wt% Ru in the final catalyst), confirming the good dispersion of Ru on all support surfaces (Table 2).





**Fig. 1** Tomographic analysis of the RuO<sub>2</sub>/TiO<sub>2</sub>-P25 sample before calcination. (a) STEM-HAADF image extracted from the tilt series used to calculate the reconstruction of this aggregate. (b) 3D model of the studied aggregate, showing TiO<sub>2</sub> in light grey, RuO<sub>2</sub> nanoparticles in red, and gold nanoparticles deposited on the TEM membrane for alignment purposes in yellow. (c) Representative slices extracted from the reconstruction. The RuO<sub>2</sub> nanoparticles are pointed by red arrows. A video showing the reconstructed volume with the catalyst particles deposited on the P25 TiO<sub>2</sub> support under rotation is available in the ESI† (SI-4).

**Table 1** Summary of specific surface areas (*S*<sub>BET</sub>)

Annealing temperature (°C)	RuO <sub>2</sub> /TiO <sub>2</sub> -P25 (m <sup>2</sup> g <sup>-1</sup> )	RuO <sub>2</sub> /TiO <sub>2</sub> -A (m <sup>2</sup> g <sup>-1</sup> )	RuO <sub>2</sub> /TiO <sub>2</sub> -R (m <sup>2</sup> g <sup>-1</sup> )
Pristine support	50	139	71
150	52	132	64
250	45	118	60
350	50	64	41
450	46	60	32

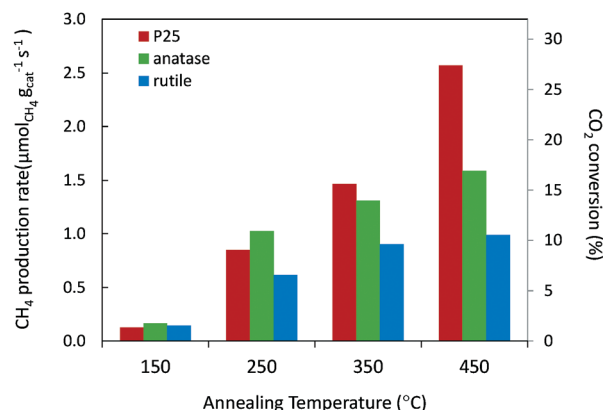
**Table 2** XPS analysis results of RuO<sub>2</sub>/TiO<sub>2</sub> catalysts after annealing. The Ru signal is deconvoluted as the oxidized (ox) and metallic (met) components

References	Ru at%		Ti at%	Ru/Ti
	ox	met		
RuO <sub>2</sub> /TiO <sub>2</sub> -P25-150	1.90	0.04	19.66	0.099
RuO <sub>2</sub> /TiO <sub>2</sub> -P25-250	0.52	0.99	20.05	0.075
RuO <sub>2</sub> /TiO <sub>2</sub> -P25-350	0.49	0.43	20.07	0.045
RuO <sub>2</sub> /TiO <sub>2</sub> -P25-450	0.35	0.32	20.31	0.033
RuO <sub>2</sub> /TiO <sub>2</sub> -A-150	0.85	0.07	20.38	0.045
RuO <sub>2</sub> /TiO <sub>2</sub> -A-250	0.91	0.08	20.88	0.047
RuO <sub>2</sub> /TiO <sub>2</sub> -A-350	0.87	1.06	19.54	0.098
RuO <sub>2</sub> /TiO <sub>2</sub> -A-450	0.44	0.69	20.37	0.055
RuO <sub>2</sub> /TiO <sub>2</sub> -R-150	0.96	0.17	21.15	0.053
RuO <sub>2</sub> /TiO <sub>2</sub> -R-250	1.06	0.12	20.33	0.058
RuO <sub>2</sub> /TiO <sub>2</sub> -R-350	0.66	0.04	20.39	0.034
RuO <sub>2</sub> /TiO <sub>2</sub> -R-450	0.48	0.04	18.72	0.028

## CO<sub>2</sub> methanation activity

The RuO<sub>2</sub>/TiO<sub>2</sub> catalysts were annealed at various temperatures, reduced in the reactor to obtain metallic Ru, and then tested in CO<sub>2</sub> methanation at one atmospheric pressure and in the 50–200 °C temperature range. Under these conditions, as predicted by thermodynamic equilibrium calculations, selectivity to methane and water was always 100% for all three catalysts. The balance between converted CO<sub>2</sub> and produced CH<sub>4</sub> was always equilibrated. The specific activities of all catalysts with three supports at various annealing temperatures and reaction temperatures are provided in the ESI† (SI-6). The catalytic activities at 200 °C expressed in terms of the CH<sub>4</sub> production rate (μmol methane produced per second and per gram of the catalyst) and in terms of CO<sub>2</sub> conversion were compared for the three different TiO<sub>2</sub> supports (Fig. 2). The CH<sub>4</sub> production rate at a given reaction temperature increased with higher annealing temperatures for all three supports.

Strikingly, even if the Ru loading is strictly the same for the three studied supports, marked differences were observed in terms of activity depending on the nature of the support. The global trend (more evident as the annealing temperature increases) in terms of CH<sub>4</sub> production rates is found to be P25 > anatase > rutile. This points to a decisive role of the TiO<sub>2</sub> crystal structure in the catalytic behaviour of the final Ru/TiO<sub>2</sub> catalysts. The activation energies of the catalysts annealed at 450 °C were obtained by scanning the catalytic activities from 100 to 200 °C, and were found to be 14.3, 14.3 and 15.4 kcal mol<sup>-1</sup>, for Ru/TiO<sub>2</sub>-P25-450, Ru/TiO<sub>2</sub>-A-450 and Ru/TiO<sub>2</sub>-R-450, respectively (SI-7†). The fact that similar values of activation energies are found suggests that the active species are the same in all the catalysts, *i.e.* the TiO<sub>2</sub> crystal structure does not affect the reaction mechanism. The higher catalytic activity of P25 TiO<sub>2</sub> supported catalyst compared to anatase or rutile TiO<sub>2</sub> may therefore be attributed to



**Fig. 2** Influence of annealing temperatures and TiO<sub>2</sub> supports on CO<sub>2</sub> methanation activity at 200 °C. Under the conditions used in this study, the highest activity level reported (2.57 μmol<sub>CH<sub>4</sub></sub> g<sub>cat</sub><sup>-1</sup> s<sup>-1</sup>) corresponds to a CO<sub>2</sub> conversion of 27.4%. It is consistent with the activity levels reported by other groups (e.g. ~7.8 μmol<sub>CH<sub>4</sub></sub> g<sub>cat</sub><sup>-1</sup> s<sup>-1</sup> at 200 °C with a 5 wt% Ru/TiO<sub>2</sub> catalyst reported by Lin et al.<sup>12</sup>).





a greater number of active sites. Thus the  $\text{TiO}_2$  crystal structure must play a role in the genesis and stabilization of the active phase.

### Catalyst modifications upon annealing

Drastic morphology modifications are observed on all three catalysts after the thermal annealing, and these changes are more marked as the annealing temperature increases from 150 to 450 °C. The TEM images provided in Fig. SI-3† show that  $\text{RuO}_2$  evolves differently upon heating, depending on the crystal structure of the  $\text{TiO}_2$  support: hardly visible on P25, present as large crystals on anatase, and present as cracked thin layers on rutile. These general observations corroborate an earlier study on the growth of  $\text{RuO}_2$  on anatase and rutile  $\text{TiO}_2$ .<sup>13</sup> Importantly, while the size of the P25 particles remains constant upon heating, sintering of home-made rutile and anatase is observed by TEM (SI-8†). This is also confirmed by BET measurement (Table 1), as well as Scherrer calculation from the main diffraction peaks (SI-9†). The different sintering behavior is a factor influencing the catalytic properties. More in-depth observations at each temperature are discussed below sequentially for P25, anatase, and rutile-supported catalysts.

### P25

In P25, the anatase and rutile particles look alike, even in HR-TEM: similar shapes and numerous atomic planes presenting a  $d$  spacing below 3 Å (only the rutile 110 plane at 3.2 Å can be easily separated from the anatase 101 plane at 3.5 Å).

As the calcination temperature increased from 150 °C (Fig. 4a) to 250, 350, and 450 °C, the  $\text{RuO}_2$  nanoparticles – initially clearly visible – became difficult to observe in HR-TEM (weaker contrast, disappearance of the  $\text{RuO}_2$  nanoparticles). After annealing at 250 °C, the TEM images revealed a tendency of  $\text{RuO}_2$  nanoparticles to aggregate in the form of layers (Fig. SI-10†). A darker layer around some  $\text{TiO}_2$  particles was observed (2–3 nm thick), corresponding to the detection of ruthenium by EDX spectroscopy, whereas Ru was absent elsewhere (EDX analysis spot is ~100 nm). The inter-atomic spacing of the crystal lattice of this particle was measured to be around 3.2 Å, which is consistent with the (110) plane of rutile  $\text{TiO}_2$  (3.24 Å) as well as the (110) plane of  $\text{RuO}_2$  (3.18 Å). Thus, a  $\text{RuO}_2$  thin layer is seen on rutile  $\text{TiO}_2$  particles. This  $\text{RuO}_2$  redistribution phenomenon during thermal treatment or catalysis has also been proposed in the decon process as well as total oxidation reactions.<sup>13,30</sup>

High-angle annular dark-field (HAADF) and bright field images were taken by scanning transmission electron microscopy (STEM) in order to obtain higher Z-contrast images of the 450 °C heated catalyst (Fig. 4b–f). Remarkably, the white spots and layers found in dark-field images were found only on rutile  $\text{TiO}_2$  particles. Energy dispersive X-ray spectroscopy (EDX) clearly identified those white spots as being Ru-rich. A higher atomic concentration of Ru was detected surrounding

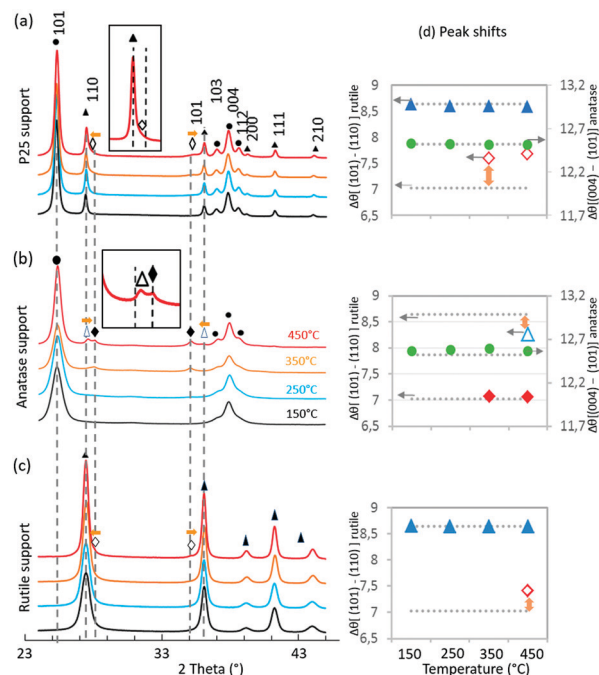


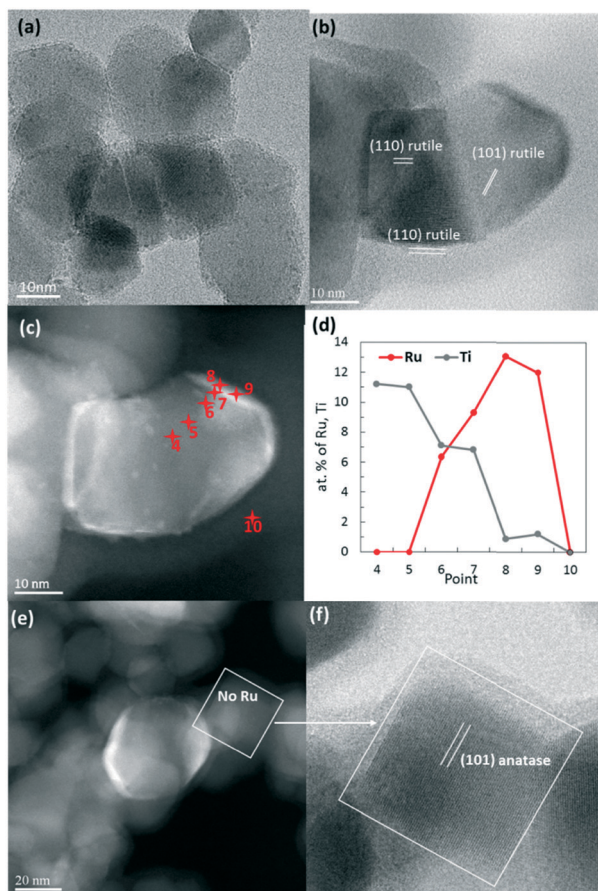
Fig. 3 XRD patterns of the catalysts annealed at different temperatures. P25 support (a), anatase support (b) and rutile support (c). The vertical dotted grey lines represent the expected peaks based on ICDD (021-1276  $\text{TiO}_2$  rutile, 021-1272  $\text{TiO}_2$  anatase and 043-1027  $\text{RuO}_2$ ); experimental peaks are assigned to  $\text{TiO}_2$  anatase (●),  $\text{TiO}_2$  rutile (▲), shifted  $\text{TiO}_2$  rutile (Δ),  $\text{RuO}_2$  (◆) and shifted  $\text{RuO}_2$  (◇). For each phase, the difference has been calculated between the  $2\theta$  positions of the 2 main peaks. (d) The horizontal dotted grey lines represent the corresponding calculated values from ICDD.

the rutile  $\text{TiO}_2$  particles, suggesting the presence of a  $\text{RuO}_2$  layer (Fig. 4c and d). The anatase  $\text{TiO}_2$  particles, which represent 80% of the P25 support, remained completely free of Ru (Fig. 4e and f).

Consistent with TEM observations, XRD analysis and Scherrer calculations showed that the crystallinity of P25 does not evolve with the increased annealing temperature of the catalyst (Fig. 3a and ESI† SI-9 and SI-11).

The  $\text{TiO}_2$  diffraction peaks (both anatase and rutile phases) do not shift in position at all annealed temperatures. Deconvolution of  $\text{RuO}_2$  peaks, however, showed that, with increased annealing temperature, the (110)  $\text{RuO}_2$  and (101)  $\text{RuO}_2$  peaks shift in opposite directions, both towards the associated (110) and (101) rutile  $\text{TiO}_2$  peaks. This is particularly clear in Fig. 3d where  $\Delta\theta[(101)-(110)]$  is higher than the expected value from ICDD for  $\text{RuO}_2$ . This observation is a clear indication of epitaxial interactions between  $\text{RuO}_2$  and rutile  $\text{TiO}_2$  and is supported by the fact that  $\text{RuO}_2$  and rutile  $\text{TiO}_2$  present the same rutile crystal structure with very close lattice parameters (for rutile  $\text{TiO}_2$ ,  $a = 4.5933$  Å,  $c = 2.9592$  Å – 021-1276; and for  $\text{RuO}_2$ ,  $a = 4.4994$  Å,  $c = 3.1071$  Å – 043-1027). Indeed, the degree of mismatch between the pure reference  $\text{RuO}_2$  and the pure rutile reference  $\text{TiO}_2$  stands at 1.8% for the (110) surface and 2.7% for the (101) surface, values that are largely below the reported 5% limit allowing





**Fig. 4** RuO<sub>2</sub>/TiO<sub>2</sub>-P25 heated at 150 °C (a) and 450 °C (b–f). STEM-BF (bright field) micrograph (b) of an identified rutile P25 particle and the corresponding STEM-HAADF image (c) revealing RuO<sub>2</sub> as white layers and particles. EDX analysis (d) was performed on 10 chosen spots (as indicated by the red points) to verify that the Ru concentration is high on the white areas. A HAADF image (e) showing a naked particle and a zoomed-in image corresponding to the bright field image (f) identifying this particle as anatase.

epitaxial layer growth. As discussed in detail in the ESI† (SI-12), the shift in RuO<sub>2</sub> peak positions towards rutile TiO<sub>2</sub> peak positions has consequences on the RuO<sub>2</sub> structure. The epitaxial growth of RuO<sub>2</sub> on rutile TiO<sub>2</sub> implies that the RuO<sub>6</sub> octahedra are less distorted compared to RuO<sub>6</sub> octahedra from the RuO<sub>2</sub> crystal alone.

XPS analysis showed a decrease in the atomic ratio of Ru/Ti with the increase in annealing temperatures (Table 2). This corroborates the sintering or concentration of RuO<sub>2</sub> on rutile TiO<sub>2</sub> particles as previously discussed based on the TEM observations.

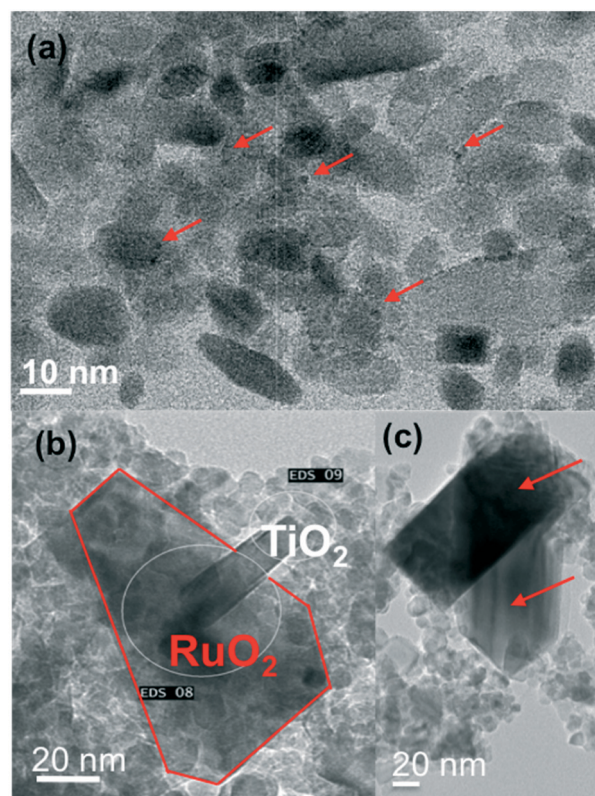
### Anatase

The  $S_{\text{BET}}$  of the RuO<sub>2</sub>/TiO<sub>2</sub>-A catalyst decreased drastically by annealing from 150 to 450 °C, indicating the occurrence of support sintering. This trend was well correlated with TEM observations.

RuO<sub>2</sub> appeared relatively well dispersed at 150 °C (Fig. 5a). TEM and EDX on various regions show that this remained

the case at 250 °C (SI-13a†). After annealing at 350 °C or 450 °C, some large dark crystals were found among the smaller TiO<sub>2</sub> anatase particles (Fig. 5b). EDX confirmed that a large part of the TiO<sub>2</sub> surface was free of Ru and that the large dark crystals were RuO<sub>2</sub> (SI-13b†). Interestingly, rod-shaped crystals were also observed and identified as TiO<sub>2</sub> rutile rods (Fig. 5b and SI-13c†). Crystallization of TiO<sub>2</sub> rutile has been triggered by the rutile RuO<sub>2</sub> structure, leading to anatase-to-rutile transformation at temperatures significantly lower than the usual ~600 °C.<sup>34,35</sup> Contrary to the case of the rutile phase of P25, RuO<sub>2</sub> does not migrate toward the newly grown rutile TiO<sub>2</sub> crystal.

From XRD analysis (Fig. 3b), the pure anatase TiO<sub>2</sub> peaks became narrower with increased annealing temperature consistent with the increase in crystal size (SI-9†). Deconvolution of the RuO<sub>2</sub> peaks was only possible from 350 °C (SI-11†). RuO<sub>2</sub> peaks appeared at the expected position for rutile RuO<sub>2</sub> (Fig. 3d). This is in relation with TEM images where large RuO<sub>2</sub> crystallites were observed to be clearly separated from the anatase TiO<sub>2</sub> support. At 350 °C and 450 °C, (110) and (101) rutile TiO<sub>2</sub> peaks were observed, with a satisfactory deconvolution only possible at 450 °C. Interestingly, these



**Fig. 5** TEM images of the RuO<sub>2</sub>/TiO<sub>2</sub>-A catalyst after annealing at 150 °C (a), 350 °C (b) and 450 °C (c); at 150 °C, RuO<sub>2</sub> particles are relatively well dispersed (a) whereas large RuO<sub>2</sub> nanocrystals crystallize separately from TiO<sub>2</sub> anatase at 350 °C and 450 °C (b and c, respectively). TiO<sub>2</sub> rutile also crystallizes from RuO<sub>2</sub> crystals. The RuO<sub>2</sub> phase is pointed by red arrows or lines. The white circles show the areas where EDX has been performed to confirm the identification of the crystals (SI-13†).



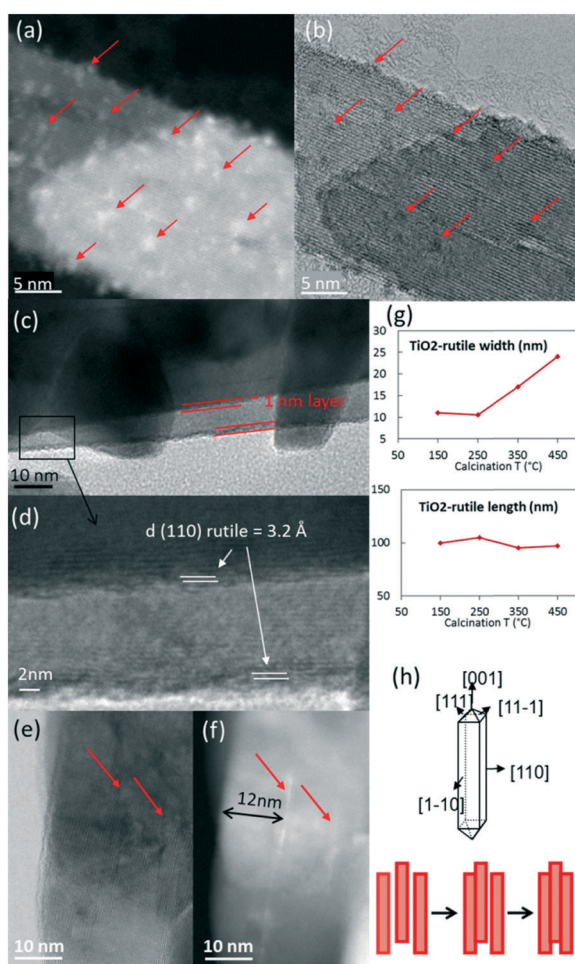


rutile  $\text{TiO}_2$  peaks were identified as (110) and (101)  $\text{TiO}_2$  rutile peaks shifted, respectively, towards (110) and (101)  $\text{RuO}_2$  peaks. This observation indicates the occurrence of rutile  $\text{TiO}_2$  crystallization starting at 350 °C through the epitaxial lattice matching mechanism from  $\text{RuO}_2$  to  $\text{TiO}_2$ .

XPS analysis showed that the Ru/Ti ratios remained similar for different annealing temperatures with the exception of the 350 °C annealed catalyst. Due to the sintering of both support and Ru species on the pure anatase support, establishment of a reliable trend at various annealing temperatures becomes critical.

## Rutile

TEM observations showed a gradual evolution of  $\text{RuO}_2/\text{TiO}_2\text{-R}$  catalysts with increasing annealing temperatures (ESI† SI-14 and Fig. 6).



**Fig. 6** STEM-HAADF (a) and STEM-BF images (b) of  $\text{RuO}_2/\text{TiO}_2\text{-R}$  heated at 150 °C.  $\text{RuO}_2/\text{TiO}_2\text{-R}$  heated at 450 °C (c–f) showing the 110  $\text{RuO}_2$  and  $\text{TiO}_2$  rutile planes (c and d) as well as the thin  $\text{RuO}_2$  layers in the bright field image (e) and the corresponding HAADF image (f).  $\text{TiO}_2$  rutile particle size evolution with temperature (g) allows the development of a schematic drawing (h) of  $\text{TiO}_2$ -rutile growth in the direction of the (110) facet. The red arrows point at  $\text{RuO}_2$ .

After annealing at 150 °C, the  $\text{RuO}_2$  nanoparticles were well distributed on the intact rod-shaped rutile  $\text{TiO}_2$  particles (Fig. 6a and b).

Starting from 250 °C, the nanoparticles started to evolve into thin  $\text{RuO}_2$  layers. With increasing annealing temperature, the ~1 nm thick layer around the rutile  $\text{TiO}_2$  rods became better defined. The thin layer was verified to have a  $d$ -spacing of 3.2 Å, which corresponds to the (110) plane of rutile  $\text{RuO}_2$  (3.18 Å) (Fig. 6c and d). This is an indication that the (110)  $\text{RuO}_2$  plane is oriented parallel to the (110) rutile  $\text{TiO}_2$  plane of the support, forming the so-called epitaxial layer, similar to that on the rutile particles of P25.

The support itself was clearly affected by the thermal treatment (Fig. 3c and SI-8†). The width of the support particles was found to be approximately doubled from 150 °C to 450 °C (also confirmed by Scherrer calculations, SI-9†), while the length remained constant. It suggests stacking of the rod-shaped rutile  $\text{TiO}_2$  particles in the direction of the (110) facet, as depicted in Fig. 6g and h. The STEM-BF images and their corresponding HAADF images revealed the presence of white lines of  $\text{RuO}_2$  layers every ~12 nm on average, which corresponds to the initial width of the rutile  $\text{TiO}_2$  rod (Fig. 6e and f). This is evidence that  $\text{RuO}_2$  epitaxial layers on the (110) facet of rutile  $\text{TiO}_2$  act as “glue” between the 12 nm-wide  $\text{TiO}_2$  rutile rods, resulting in the “sandwiching” of the  $\text{RuO}_2$  layers between the  $\text{TiO}_2$  rods.

## Discussion on the $\text{RuO}_2$ nanoparticle migration

The redistribution process of  $\text{RuO}_2$  during heat treatment from anatase  $\text{TiO}_2$  particles to rutile  $\text{TiO}_2$  particles appears to play a major role in catalyst activation. This phenomenon only occurs for small  $\text{RuO}_2$  particles (2 nm or smaller).<sup>13</sup> In this size range, surface tension dominates most physico-chemical properties of nanomaterials, especially the interface behaviour and surface stability.  $\text{RuO}_2$  arrival on rutile  $\text{TiO}_2$  is clearly driven by epitaxy stabilization. The departure of the ruthenium atoms from the anatase  $\text{TiO}_2$  surface is more controversial. Two possible pathways are proposed:  $\text{RuO}_2$  local volatilization ( $\text{RuO}_3$  and  $\text{RuO}_4$ ) followed by redeposition<sup>36–38</sup> and  $\text{RuO}_2$  nanoparticle diffusion.<sup>39,40</sup> As discussed in detail in the ESI† (SI-20), it is difficult to totally exclude one of the two mechanisms. The fact that the Ru loading remains constant from  $\text{RuO}_2$  deposition until after the catalytic test indicates that volatilization is unlikely. This is also further supported by thermodynamic calculations.<sup>41</sup> In any case, if volatilization occurs, it has to remain local (volatilization followed by immediate re-deposition). We rather propose that small  $\text{RuO}_2$  nanoparticles diffuse at the surface of the  $\text{TiO}_2$  particles, driven by the Ostwald ripening mechanism, as it is well documented in the literature.<sup>42–44</sup> Subsequently, the diffusion of  $\text{RuO}_2$  nanoparticles leads to two different phenomena in terms of sintering: isotropic growth of  $\text{RuO}_2$  crystals on the pure anatase  $\text{TiO}_2$  support or epitaxial growth of the  $\text{RuO}_2$  layer on rutile  $\text{TiO}_2$  (P25 and pure rutile  $\text{TiO}_2$  supports).



### Catalyst modifications upon reduction

A close observation of the morphology of the  $\text{RuO}_2$  phase at different annealing temperatures indicated unambiguously that the nature of the support dictates the behaviour of the  $\text{RuO}_2$  nanoparticles, and this was correlated with different catalytic performances. Yet, the actual active species in the methanation reaction are the reduced states of Ru over  $\text{TiO}_2$  obtained after an *in situ* thermal treatment under  $\text{H}_2$  at 200 °C.

The three most active catalysts for each support, annealed at 450 °C, were analysed by conducting TPR (SI-15†). The  $\text{H}_2$  consumption profiles for the three catalysts were not overlapping, thus confirming the strong impact of the support structure. For the P25 supported catalyst, two close reduction events were observed, as often reported for titania-supported  $\text{RuO}_2$ .<sup>45</sup> The origin of the two reduction peaks is sometimes attributed to an inhibiting effect of residual water on the reduction kinetics.<sup>46</sup> The complex reduction profile is often attributed to a heterogeneous distribution of  $\text{RuO}_2$  particles<sup>47</sup> or to the presence of different  $\text{RuO}_2$  species which develop different types of interactions with the respective  $\text{TiO}_2$  supports.<sup>45</sup> Here, the oxidized Ru species on the different  $\text{TiO}_2$  supports show very different reduction patterns, confirming that Ru species are different from the respective catalysts, probably in terms of size, accessibility, or support interaction. While reduction occurs below 200 °C on P25, for anatase and rutile, the two reduction peaks are shifted towards higher temperatures. Interestingly, by looking at the relative intensities of the reduction peaks, TPR shows that  $\text{RuO}_2$  in  $\text{Ru}/\text{TiO}_2\text{-R-450}$  is less reducible, corresponding to trapped  $\text{RuO}_2$  layers.

In  $\text{Ru}/\text{TiO}_2\text{-P25-450}$  post methanation, as  $\text{RuO}_2$  is reduced into metallic Ru, the epitaxial lattice matching over rutile  $\text{TiO}_2$  is suppressed. Additionally, the electronic density is higher in metallic ruthenium than in  $\text{RuO}_2$ . As a result, the TEM image contrast between metallic Ru and  $\text{TiO}_2$  becomes higher than that between  $\text{RuO}_2$  and rutile  $\text{TiO}_2$ . This allows one to clearly distinguish metallic Ru patches that are non-homogeneously dispersed on  $\text{TiO}_2$  P25 particles. Most  $\text{TiO}_2$  particles remain “naked” (Ru-free) and a few particles are covered by Ru nanoparticles (Fig. 7a). The HR-TEM images clearly showed (110)  $\text{TiO}_2$  rutile planes underneath Ru particles (SI-16a and b†) and 101 anatase planes on the naked  $\text{TiO}_2$  particles. 3D-TEM tomographic analysis (Fig. 8) of  $\text{Ru}/\text{TiO}_2\text{-P25-450}$  after reduction and methanation unambiguously confirms the 2D TEM observations by showing the presence of Ru particles (mean size of  $2.8 \pm 1.0$  nm) localized preferentially on the surface of rutile  $\text{TiO}_2$  particles, leaving the  $\text{TiO}_2$  anatase particles naked. A media file corresponding to the tomography analysis is uploaded in the ESI† (SI-17, after test-mix.avi). This unambiguously shows that the Ru particles that accumulated specifically onto the rutile  $\text{TiO}_2$  particles in the form of  $\text{RuO}_2$  epitaxial layers during annealing remain localized over the same  $\text{TiO}_2$  rutile particles upon reduction. As observed previously during the ther-

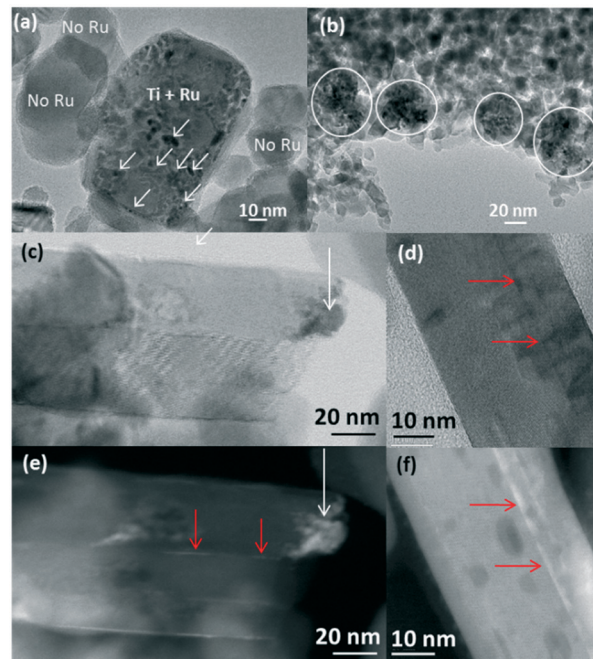


Fig. 7 TEM images of the catalysts post reduction and methanation: (a)  $\text{Ru}/\text{TiO}_2\text{-P25-450}$  post methanation showing Ru-free anatase  $\text{TiO}_2$  and Ru-covered rutile  $\text{TiO}_2$  particles; (b)  $\text{Ru}/\text{TiO}_2\text{-A-450}$  post methanation showing agglomerated Ru particles (indicated by white circles); bright field (c and d) and HAADF (e and f) images of  $\text{Ru}/\text{TiO}_2\text{-R-450}$  post methanation. The white arrows show the metallic Ru, and the red arrows show the trapped  $\text{RuO}_2$ .

mal annealing treatment, the mean particle size of  $\text{TiO}_2$  P25 has not been affected by the catalytic test and remained at  $25 \pm 14$  nm.

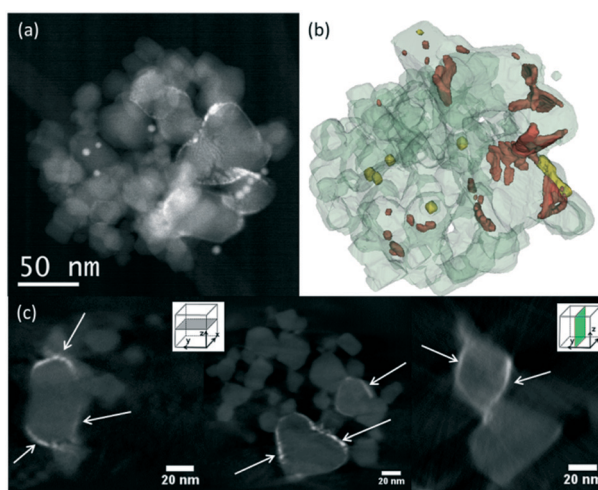


Fig. 8 3D-TEM tomographic analysis of  $\text{Ru}/\text{TiO}_2\text{-P25-450}$  after reduction and the catalytic test showing the presence of Ru particles on the surface of rutile  $\text{TiO}_2$  particles. (a) STEM-HAADF image showing the particle aggregate used for 3D reconstruction, (b) volume reconstruction of the studied aggregate, with Ru nanoparticles in red,  $\text{TiO}_2$  in light grey and Au nanoparticles used for tomogram alignment in yellow. (c) Representative slices extracted from the reconstruction. Ru particles are pointed by the white arrows.





On the anatase support, metallic Ru particles appear as agglomerates of smaller particles, as shown in Fig. 7b. The approximate sizes of these agglomerates are in the same range as that of the RuO<sub>2</sub> crystal prior to reduction and the catalytic test (50 to 100 nm). It is suggested that RuO<sub>2</sub> has undergone fragmentation during reduction, but no significant re-dispersion, leaving most of the anatase particles uncovered. The Ru particles appear crystalline (100, 002 and 101 planes of metallic Ru) (SI-16c and d†), with a mean size of  $3.8 \pm 1.0$  nm. As observed on the non-reduced sample, a few rutile TiO<sub>2</sub> crystals could be seen, systematically decorated with Ru particles (SI-16c†), again attesting the absence of Ru mobility during reduction and methanation. The size of anatase TiO<sub>2</sub> particles remains unchanged after reduction and methanation ( $11.5 \pm 2.6$  nm).

On pure rutile TiO<sub>2</sub>, metallic crystalline Ru particles can be easily seen after methanation (Ru planes observed on SI-16e and f†); they are mainly localized close to the tip of the TiO<sub>2</sub> rutile needles (Fig. 7c and e). Their mean size is  $3.5 \pm 1.0$  nm. The TiO<sub>2</sub> needles have not sintered during reduction or reaction (length of  $96 \pm 17$  nm and width of  $24 \pm 5$  nm). The Ru particles, however, appear scarce on the numerous images that were obtained in comparison with the P25 and anatase supports. Instead, the STEM-HAADF images show trapped Ru-containing layers in between the rutile TiO<sub>2</sub> crystals (Fig. 7c–f), indicating that the “sandwiching” of RuO<sub>2</sub> is maintained upon reduction.

XPS analysis after methanation revealed that the Ru/Ti ratios remained similar to the values obtained before methanation for all three supports (Table 3), indicating that the catalyst dispersion was barely modified after reduction and methanation. For all three supports, the proportion of surface metallic Ru increased after reduction and methanation (SI-18†). It is, however, important to note that the metallic Ru proportion on the rutile support was significantly lower compared to the P25 and anatase supports. This is explained by the “sandwiched” RuO<sub>2</sub> layers described above that are protected from H<sub>2</sub> exposure and thus reduction.

On the P25 support, the proportion of oxidized and metallic Ru in the spent catalysts was always around 40% oxidized and 60% metallic Ru species (after being exposed to air) regardless of the annealing temperature (ESI†, SI-18a and b). This indicates that the beneficial effect of a high annealing temperature is exerted through the morphological changes observed for the active phase and not through a change in reducibility of the RuO<sub>2</sub> phase.

**Table 3** Comparison of Ru/Ti ratios measured by XPS before and after reduction and methanation for catalysts annealed at 450 °C

Support	Ru/Ti (XPS)	
	Before reduction	After methanation
P25	0.033	0.036
Anatase	0.055	0.068
Rutile	0.028	0.031

H<sub>2</sub> chemisorption resulted in the Ru dispersion values of 24%, <5%, and 13% for Ru/TiO<sub>2</sub>-P25-450, Ru/TiO<sub>2</sub>-A-450, and Ru/TiO<sub>2</sub>-R-450, respectively. A lower Ru dispersion suggests sintering of Ru nanoparticles. Based on the fact that the P25 and rutile supports follow the same pattern of RuO<sub>2</sub> modification through epitaxial layer formation, the lower Ru dispersion value of Ru/TiO<sub>2</sub>-R-450 compared to Ru/TiO<sub>2</sub>-P25-450 is clearly attributed to the loss of Ru in between the rutile TiO<sub>2</sub> particles. On the other hand, the lowest Ru dispersion value of Ru/TiO<sub>2</sub>-A-450 is due to the high degree of sintering of RuO<sub>2</sub> resulting in highly agglomerated Ru after reduction. In conclusion, dispersion is strongly affected by the modifications that occur during annealing as described above.

### Decisive factors dictating the methanation activity

The catalysts prepared on different crystalline TiO<sub>2</sub> supports show distinctive behaviors in the catalytic CO<sub>2</sub> methanation. Although the selectivity to CH<sub>4</sub> was 100% for all the catalysts, the level of activity was markedly affected by the crystallinity of the TiO<sub>2</sub> support used. As a general trend, the P25 supported catalysts showed the best CH<sub>4</sub> production rate, followed by anatase- and then rutile-supported catalysts.

Taking into account the dispersion data (H<sub>2</sub> chemisorption), an apparent turnover frequency (TOF) can be calculated on the basis of the amount of Ru available at the catalyst surface. At 200 °C, the TOF (expressed as mole of CH<sub>4</sub> produced per mole of surface-accessible Ru per second) reached  $\sim 7$  s<sup>-1</sup> for both Ru/TiO<sub>2</sub>-P25-450 and Ru/TiO<sub>2</sub>-R-450. This indicates that the specific activity of P25 and rutile-supported catalysts is directly related to the dispersion of the Ru phase. The TOF is found to be higher for Ru/TiO<sub>2</sub>-A-450 (about 43 s<sup>-1</sup>). This suggests that different Ru species exist on the anatase TiO<sub>2</sub> support, exhibiting a higher density of active sites compared to those stabilized onto P25 or rutile TiO<sub>2</sub> supports. Indeed, methanation is thought to be a structure-sensitive reaction, since different physical states of active species have been reported to have different intrinsic activities. The importance of size and size distribution for the active nanoparticles has been proven in the case of ammonia synthesis (Ru particles) and CO<sub>2</sub> methanation (Rh particles) under mild conditions.<sup>48–50</sup> Moreover, the role of the exposed active face, defects, steps or terraces on the catalyst surface has been widely discussed for Ru/TiO<sub>2</sub> catalysts.<sup>51</sup>

In both commonly proposed pathways for CO<sub>2</sub> methanation (*i.e.* via formate intermediates or by direct CO<sub>2</sub> dissociation into CO(ads) and O(ads)), the dissociation of CO(ads) is generally recognized to be the rate-determining reaction and is expected to proceed at different rates on different Ru surface species.<sup>21,52,53</sup>

As recently confirmed by near ambient pressure X-ray photoelectron spectroscopy, the active state of ruthenium is the metallic one.<sup>54</sup> Yet the level of performance is dictated by the state of the catalyst after annealing. Detailed TEM observations of the catalyst after various annealing temperatures





provide a link between the morphology and the catalytic behaviour (Fig. 9). In summary, on anatase and rutile  $\text{TiO}_2$  phases, two main phenomena occur during annealing, both driven towards the stabilization of the system: intrinsic growth of the particles and  $\text{RuO}_2$ - $\text{TiO}_2$  epitaxy. Concerning anatase, the weak interaction between  $\text{RuO}_2$  and anatase  $\text{TiO}_2$  results in the growth of large rutile  $\text{RuO}_2$  crystals, as well as separate  $\text{TiO}_2$  anatase sintering. After reduction, the resulting large metallic Ru aggregates have low proportions of surface Ru (detected by  $\text{H}_2$  chemisorption) which translates into modest levels of specific methanation activity, despite a higher TOF. Concerning the rutile support, the strong interaction between  $\text{RuO}_2$  and rutile  $\text{TiO}_2$  promotes the formation of continuous epitaxial layers, dominantly over the (110) facet. A “sandwiching” phenomenon is also observed, concomitantly with  $\text{TiO}_2$  rutile sintering (increase in particle width). This results in the loss of Ru species, embedded between  $\text{TiO}_2$  rods. The low activity of the rutile supported catalyst is explained by this embedding of the active phase. The P25 particles do not sinter and the stabilization occurs through  $\text{RuO}_2$ -rutile  $\text{TiO}_2$  epitaxial interactions.  $\text{RuO}_2$  is thus spread on the  $\text{TiO}_2$  rutile surface, with anatase particles acting as the diluent and preventing the  $\text{TiO}_2$  rutile- $\text{RuO}_2$ - $\text{TiO}_2$  rutile stacking. With a high amount of Ru available at the surface, as compared to the catalyst supported on pure rutile,  $\text{Ru}/\text{TiO}_2$ -P25-450 presents the highest specific activity.

## Conclusions

$\text{Ru}/\text{TiO}_2$  methanation catalysts were studied systematically, starting from calibrated  $\text{RuO}_2$  nanoparticles as the precursor

for active Ru species, which are subsequently supported on anatase, rutile, and a mixture of the two (P25) crystal structures of  $\text{TiO}_2$ . Different crystalline  $\text{TiO}_2$  as supports for  $\text{RuO}_2$  nanoparticles are shown to have a marked impact on catalytic performance. This is rationalized by studying how the physico-chemical properties of the catalyst's active phase depend on the crystalline structure of the support.

We show that the annealing step provokes intense modifications of the catalyst properties. These modifications are strongly dependent on the crystal structure of the support. The weak interactions between  $\text{RuO}_2$  and anatase  $\text{TiO}_2$  cause sintering and growth of  $\text{RuO}_2$  crystals, whereas the strong interactions (*i.e.* lattice-matched interfacial structure) between the  $\text{RuO}_2$  and rutile  $\text{TiO}_2$  lead to a transformation of nanoparticles into epitaxial  $\text{RuO}_2$  layers sandwiched between rutile  $\text{TiO}_2$  rods. In both cases, the specific activity is decreased, either because the amount of surface accessible Ru drops significantly. On the surface of P25  $\text{TiO}_2$ , the mixing of anatase and rutile particles gives rise to a more favourable situation where Ru does interact strongly with rutile but remains fully accessible.

These results provide an insight into the design of supported catalysts taking into account the possibility of balancing  $\text{RuO}_2$ - $\text{TiO}_2$  interactions in a favourable way. The present study should prompt further work on the tuning of the anatase/rutile ratio in search of higher catalytic activity not only in  $\text{CO}_2$  methanation but also in various catalytic reactions.

## Experimental section

### Catalyst preparation

Pure anatase  $\text{TiO}_2$  particles were prepared by microwave hydrothermal treatment at 200 °C for 2 h of an aqueous solution of  $\text{TiCl}_4$  with the acidity adjusted to pH 6. The resultant precipitates were collected by centrifugation and then washed with water and nitric acid.<sup>55</sup>

Pure rutile  $\text{TiO}_2$  particles were obtained by refluxing at 120 °C for 3 days an aqueous solution of  $\text{TiCl}_4$  in 1 M HCl followed by washing the resultant precipitates with water and nitric acid.<sup>56</sup>

A highly stable colloidal suspension of monodispersed  $\text{RuO}_2$  nanoparticles was obtained by dropwise addition of 15% v/v  $\text{H}_2\text{O}_2$  diluted in  $\text{H}_2\text{O}$  into 0.011 M  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  ( $x = 3-5$ ) dissolved in  $\text{H}_2\text{O}$  so that the final concentration is  $[\text{Ru}] \approx 0.007$  M. The solution was heated at 95 °C for 2 h. Once cooled to room temperature, an appropriate amount of  $\text{TiO}_2$  powder (P25 from Degussa, home-made pure anatase or home-made pure rutile) was added to the colloidal suspension of  $\text{RuO}_2$  nanoparticles to yield 2.5 wt% of Ru in the final catalyst. The mixture was put in an oven at 50 °C overnight and the excess water was removed by rotary evaporation. The resulting powder was then annealed/calcined at 150, 250, 350, or 450 °C for 16 h in static air and washed 3 times with water. The catalysts are denoted as  $\text{RuO}_2/\text{TiO}_2$ -P25,  $\text{RuO}_2/\text{TiO}_2$ -A, and  $\text{RuO}_2/\text{TiO}_2$ -R for P25, pure anatase, and pure

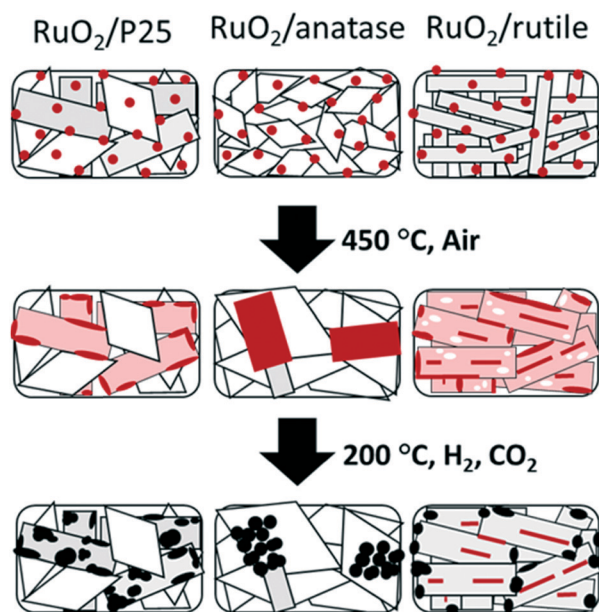


Fig. 9 Graphical illustration of the shape evolution of the  $\text{RuO}_2/\text{TiO}_2$  catalysts; after  $\text{RuO}_2$  nanoparticle deposition, after thermal annealing at 450 °C, and after reduction and methanation. Red indicates  $\text{RuO}_2$ , pink indicates thin  $\text{RuO}_2$  layers, white indicates Ru depleted areas, and black indicates metallic Ru.



rutile  $\text{TiO}_2$  supported  $\text{RuO}_2$ , respectively. After reduction under continuous flow of  $\text{H}_2$  at 200 °C (see section 2.3), the catalysts were denoted as  $\text{Ru}/\text{TiO}_2\text{-P25}$ ,  $\text{Ru}/\text{TiO}_2\text{-A}$ , and  $\text{Ru}/\text{TiO}_2\text{-R}$ , respectively. Different calcination temperatures are indicated with extended numerical notations, *e.g.*  $\text{RuO}_2/\text{TiO}_2\text{-P25-150}$ .

### Catalyst characterization

Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai 120 Twin microscope operating at 120 kV and equipped with a Gatan Orius CCD numeric camera. The samples were prepared by ultrasonic dispersion of the powders in water and a droplet of the dispersion was then placed onto a carbon-coated copper grid.

High-resolution analysis (HR-TEM) images were obtained by using a JEOL JEM 2010 microscope operating at 200 kV and equipped with a Gatan camera. The sample preparation was the same as in TEM sample preparation.

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were obtained using a Jeol 2200FS microscope equipped with a spherical aberration corrector on the probe and an EDX system from Jeol. The convergence semi-angle of the probe was 30 mrad and the current was 150 pA. The inner and the outer semiangles for the dark-field detector (upper DF detector) were 100 and 170 mrad, respectively.

3D TEM tomography data were acquired using a JEOL 2100F electron microscope. The acquisition of bright field (BF) and dark field (DF) tilt series was carried out simultaneously in scanning mode (STEM). A camera length of 10 cm was chosen for this experiment. It corresponds to inner and outer semiangles of 60 and 160 mrad, respectively, for the HAADF detector. A 100  $\mu\text{m}$  condenser aperture was employed, allowing one to reach a probe diameter of about 0.12 nm with a current density of 0.5 pA  $\text{\AA}^{-2}$ . Under these conditions, the tomography series were acquired using Digital Micrograph software (tomography plugin), giving access to an automatic increment of the tilt angles and sharp control of the specimen drift and defocusing. A high tilt specimen holder from Gatan was employed for a tilting range of  $-65^\circ$  to  $65^\circ$ , with an equal angular step of  $2.5^\circ$ .

The precision of these nanoscale 3D analyses greatly benefits from the DART reconstruction method that minimizes the artefacts due to the missing wedge. Indeed, after the fine alignment of all projections, the 3D volume was calculated using the discrete algebraic reconstruction technique (DART). For this purpose, a preliminary simultaneous iterative reconstruction technique (SIRT) reconstruction was performed. By constraining the reconstruction volume with a mask which roughly equals the particle shapes, reliable material densities can be deduced. Subsequently, the density of the gold particles is used to perform a DART reconstruction, which is discrete in terms of grey values.<sup>57</sup> This means that each voxel (unit fragment of the volume) is attributed to either vacuum

or gold. Consequently, DART is superior to SIRT when exact particle boundaries are to be determined.<sup>58</sup>

X-ray diffraction (XRD) measurements were performed with Cu  $K\alpha$  radiation using a Bruker D8 Advance diffractometer equipped with a Lynx eye detector. The  $2\theta$  diffractograms were recorded between  $24\text{--}50^\circ$  with a step size of  $0.04^\circ$  and a steep time of 20 s per step. The ICDD-PDF2 database was used to identify the crystalline phases. When possible,  $\text{TiO}_2$  and  $\text{RuO}_2$  XRD peaks were deconvoluted, using WinPLOTR.<sup>59</sup> The Scherrer equation was used to calculate the crystallite size of particles ( $\text{SI-19}^\dagger$ ).<sup>60</sup>

X-ray photoelectron spectroscopic (XPS) analyses were performed using an SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatised micro focused Al X-ray  $K\alpha$  source (powered at 20 mA and 10 kV), a  $30^\circ$  solid angle acceptance lens, a hemispherical analyser and a position-sensitive detector. The samples were pressed in small stainless steel troughs of 4 mm diameter and placed on a multi-specimen holder. The pressure in the analysis chamber was around 10–6 Pa. The angle between the surface normal and the axis of the analyser lens was  $55^\circ$ . The analysed area was approximately 1.4  $\text{mm}^2$  and the pass energy was set at 150 eV. Atomic concentration ratios were calculated by normalizing surface area ratios with sensitivity factors based on Scofield cross-sections. In addition, all binding energies were calculated taking as reference the C–(C, H) component of the C 1s adventitious carbon peak fixed at 284.8 eV. Peak decomposition was performed using the CasaXPS program (Casa Software Ltd., UK) with a Gaussian/Lorentzian (85/15) product function and a Shirley non-linear sigmoid-type baseline. The following peaks were used for the quantitative analysis: O 1s, C 1s, Ti 2p, and Ru 3d. The 3d Ru peak was decomposed into 3 doublets assigned to  $\text{Ru}^0$ ,  $\text{Ru}^{4+}$  and the related  $\text{RuO}_2$  plasmon species, respectively.<sup>61</sup> The positions of these species have been imposed at  $280.0 \pm 0.1$  eV,  $291.0 \pm 0.1$  eV and  $282.8 \pm 0.1$  eV, respectively. The binding energy difference between the 3/2 and 5/2 contributions of each doublet was fixed to 4.17 eV. Besides, the  $\text{Ru}_{3d_{3/2}}/\text{Ru}_{3d_{5/2}}$  ratio was fixed to 0.667. The FWHM of each component was limited at 2.5 eV.

TPR experiments were performed using 100 mg of each catalyst after *in situ* purging under an inert gas (Ar) at 140 °C for one hour. The analysis was carried out under 2.5 v/v%  $\text{H}_2$  diluted in inert gases (2.5:82.5:15 v/v%  $\text{H}_2$ :He:Ar) in a stream of 20  $\text{mL min}^{-1}$  from 20 °C to 500 °C using a  $5^\circ\text{C min}^{-1}$  temperature ramp.  $\text{H}_2$  consumption and  $\text{H}_2\text{O}$  production were measured simultaneously *via* a QMG 311 quadrupole mass spectrometer (Balzers) coupled in line with the reactor.

The weight percentages of Ru and Ti inside the catalysts were measured by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) using an ICAP 6500 from Thermo Scientific. The materials were dried at 105 °C before the measurement.

The specific surface area of the catalysts was obtained by means of a nitrogen adsorption–desorption isotherm





collected at  $-196\text{ }^{\circ}\text{C}$  using a BELSORB-mini II (BEL Japan, Inc.). The samples were outgassed overnight at  $140\text{ }^{\circ}\text{C}$  prior to analysis.  $S_{\text{BET}}$  was calculated by the Brunauer–Emmett–Teller (BET) method at the  $\text{N}_2$  relative pressure range of  $0.05 < P/P_0 < 0.30$ .

$\text{H}_2$  chemisorption at  $100\text{ }^{\circ}\text{C}$  was used to measure the exposed Ru atoms using an ASAP 2010C apparatus from Micromeritics. A catalyst with a weight between 150–200 mg was loaded into a Pyrex tube, and subsequently degassed under He at  $150\text{ }^{\circ}\text{C}$  for 30 min. After evacuation, the sample was reduced under pure  $\text{H}_2$  at  $200\text{ }^{\circ}\text{C}$  for 2 h (same as *in situ* reduction for methanation, see section 2.3) followed by purging with He at  $100\text{ }^{\circ}\text{C}$  for 1 h and adsorption of  $\text{H}_2$ . Two isotherms were measured in the range of 0.08–95 kPa. The first accounts for reversible and irreversible chemisorption. The sample was evacuated to desorb reversibly adsorbed  $\text{H}_2$ . The second isotherm was then measured which accounts only for the reversibly adsorbed  $\text{H}_2$ . The subtraction of the linear part of the two isotherms gave the total amount of irreversibly adsorbed (chemisorbed)  $\text{H}_2$ . The amount of surface Ru atoms was calculated from the amount of chemisorbed  $\text{H}_2$ , assuming that the chemisorption stoichiometry is  $\text{H}:\text{Ru} = 1$ .<sup>62,63</sup> Dispersion is defined as surface Ru atoms divided by total Ru atoms in the catalyst.

### Methanation of carbon dioxide

200 mg of a catalyst with a particle size between 100 and  $315\text{ }\mu\text{m}$  was loaded in a continuous flow fixed bed reactor and reduced *in situ* at  $200\text{ }^{\circ}\text{C}$  for 2 h under  $30\text{ ml min}^{-1}$  of  $\text{H}_2$  prior to the catalytic reaction. The reaction was carried out at 1 atm in the temperature range of 50 to  $200\text{ }^{\circ}\text{C}$  under a  $20\text{ ml min}^{-1}$  flow of a reaction mixture ( $\text{CO}_2$  (10 vol%),  $\text{H}_2$  (40 vol%) diluted in He). Each temperature was maintained for 52 min (3 GC injections). The exit gases were quantified using a gas chromatograph (Varian CP3800) equipped with Haysep Q, Molsieve 5A, and CP-Sil-5CB columns. The separated gases were detected by a flame ionization detector ( $\text{CH}_4$ ) and a thermal conductivity detector ( $\text{CO}$  and  $\text{CO}_2$ ). The analysis parameters were set so as to allow analysis every 19 min and to obtain measurements accurate within about 1% (relative) for the methane production rate (mole of methane produced per gram of catalyst per second). All transfer lines were maintained at  $110\text{ }^{\circ}\text{C}$  to avoid water condensation.

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